

**Redox State of the Earth's Mantle at 650 my BP Based on a Study of  
Dikes from SW Norway**

Senior Thesis

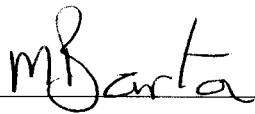
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Approved by:

A handwritten signature in black ink, appearing to read 'MBarton', is written over a horizontal line.

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## **Abstract**

The redox states of magmas, monitored by the oxygen fugacity ( $fO_2$ ), provide information about the redox states of the Earth's interior. In principle, it is possible to use oxygen fugacities for magmas erupted in different tectonic environments to map variations in the redox state of the underlying mantle. Published data indicate that the mantle source of Mid Ocean Ridge Basalts (MORB) erupted at divergent margins is reduced relative to that of magmas erupted above subduction zones. Furthermore, the oxygen fugacities of at least some Ocean Island Basalts (OIB) (eg. those from Hawaii and Iceland) are similar to that of MORB, implying derivation from mantle source regions (mantle plumes in the case of OIB) with similar redox states. Finally, many intraplate volcanics have oxygen fugacities similar to those of OIB which is consistent with derivation from mantle plumes.

The Neoproterozoic Egersund dikes in SW Norway intruded at 650-600 Ma, and the majority formed by intrusion of olivine tholeiites and tholeiites that are geochemically similar to modern OIB, in particular those from Hawaii. The magmas that intruded to form the dikes are thought to have formed from a mantle plume during the initial stages of the breakup of the supercontinent Rodinia. The rocks in the dikes are remarkably well preserved, with glassy chilled margins that contain olivine and plagioclase. Determination of the redox states of the magmas that intruded to form the dikes provides a unique opportunity to establish the redox state of plume mantle 650 my BP, and to compare these to those of magmas erupted from modern plumes.

Olivines and glasses in two dikes have been analyzed with the electron microprobe and the analyses have been used to calculate the pre-eruption temperatures and oxygen fugacities of the host magmas using a new method, based on olivine-melt equilibrium, developed at OSU. The microprobe was used to determine the compositional zoning in olivine so that the compositions, which were in equilibrium with the melt prior to eruption, could be constrained. This primarily involves examining variations in Mg/Fe between core and rim in individual olivine crystals.

Preliminary results indicate magma redox states similar to those obtained for other samples from the same dike system (ongoing research at OSU). In other words, the results obtained in this study are not anomalous, and the available data indicate that the magmas in this dike system crystallized over a narrow range of  $fO_2$ . This range is very similar to that obtained for samples from Hawaii and Iceland, indicating that the redox states of plumes have remained virtually unchanged over the past 650 my. Moreover, there is no evidence for secular variation in the redox state of the mantle over this time interval. Volcanic degassing cannot, therefore, be responsible for the increase in concentration of atmospheric oxygen that occurred at ~600 Ma. It seems more likely that this increase is related to biogenic processes or to an increase in the rate of carbon burial.

## Introduction

Geologists have the ability to study the interior of the Earth by understanding the processes and lavas formed by eruptive events. Mid Ocean Ridge Basalts (MORB) make up the upper most part of the oceanic crust. Most of the oceanic crust is subalkaline tholeiite basalt. However rare alkaline basalts and other evolved types can also exist as oceanic crust. MORB magmas potentially present the clearest view to into the mantle source. This is because MORB ascends through the thinnest and most compositionally similar crust of any tectonic setting. However, MORB does not represent a primary magma from a peridotite source [1].

Iceland is an island positioned directly over the Mid-Atlantic Ridge. It contains a central rift zone that contains recent volcanism. Due to the higher rate (one order-of magnitude-higher) of magma production than in submarine rift zones, Iceland magma must be produced by an unusually large volume of underlying hot decompressing mantle [1].

Ocean island volcanoes are more diverse in composition than MORB, which are predominately tholeiitic basalts. The mantle beneath the Hawaiian Island is not a fixed magma source, but an ascending plume [1].

The oxygen fugacity ( $fO_2$ ) monitors the redox states of magmas and can provide information about the redox state of the Earth's interior. Oxygen fugacities can be used, in principle, to record variations in the redox state of the underlying mantle for erupted magmas from

various environments. The redox state of the mantle source of MORB erupted at divergent margins is reduced relative to that of magmas erupted above subduction zones, according to published data. In other words, these contain more electrons than magmas erupted above subduction zones. Furthermore, the oxygen fugacities of, at least, some Ocean Island Basalts (OIB) from Hawaii and Iceland are similar to that of MORB. This implies derivation from mantle source regions (mantle plumes in the case of OIB) with similar redox states. Finally, many intraplate volcanics have oxygen fugacities similar to those of OIB which is consistent with derivation from mantle plumes [1].

The electron microprobe was used to constrain the composition of the olivine, which were in equilibrium with the melt prior to eruption. This involved examining variations in Mg/Fe between the core and rim values in individual olivine crystals.

## **Background**

### Regional Geology

There are three distinct regions of the Baltic Shield. They are the Archean, Svecfennian, and the SW Scandinavian. Each of these was major accretionary events during the Precambrian and is distinguished by tectonic style, metamorphic grade, and age. Outward from NE Baltica, the crustal regions get younger. Therefore, accretion of continental crust onto southwestern section of the Baltic Shield occurred [2], [3]. During the Paleoproterozoic and prior to the establishment of the supercontinent Rodinia, Baltica and Laurentia were contiguous during the Paleoproterozoic. This occurred as early as 1.9 Ga [4].

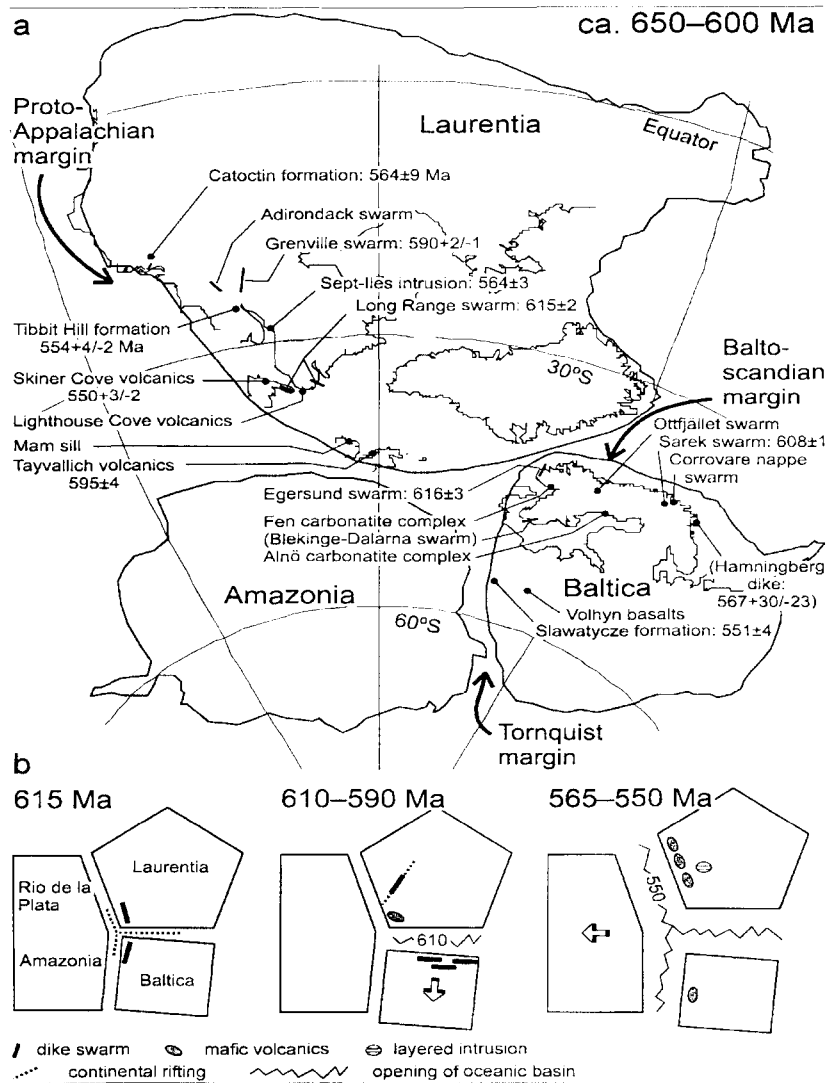
Sveconorwegian orogeny of Baltica and the later phase of the Greenville orogeny are correlated. The supercontinent Rodinia was formed out of the collision with Amazonia. Intrusive events followed the Sveconorwegian and the Greenville orogeny [5].

The breakup of Rodinia commenced along the western border of Laurentia. This led to the formation of the Proto-Pacific. Extensional tectonism began ~ 800 Ma. This was recorded by the intrusion of the Hunnedalen Dikes [6].

The final rifting event that began between Laurentia and Baltica led to the complete fragmentation of Rodinia. In addition, this event led to the formation of the Iapetus Ocean. The Egersund Dikes are a record of the initial rifting of this event [7], [8].



## Plate Reconstruction and Interpretive Sketch



[9]

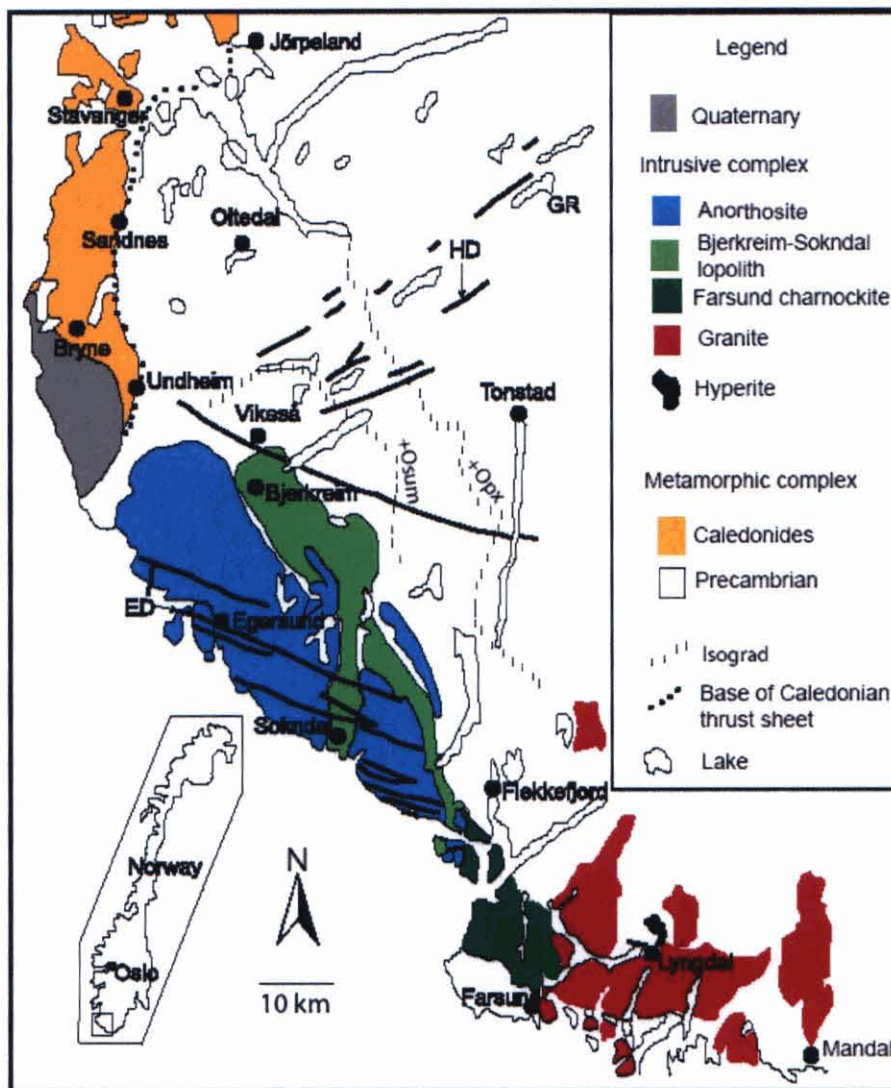
**Figure 1:** (a) Plate reconstruction at ca. 650–600 Ma according to Torsvik et al. (1996) [6] with location of Laurentia, Baltica, and Amazonia. Neoproterozoic mafic magmatic suites related to opening of Iapetus are located with zircon or baddeleyite U-Pb intrusive ages. Two suites having no direct relationship with Iapetus opening are shown between brackets. (b) Interpretative sketch map showing possible relationships between Baltica, Laurentia, and Amazonia in the interval 615–550 Ma based on time correlation of magmatic suites. Diachronic opening of Iapetus oceanic basins is suggested [3].

### Geologic Setting of the Egersund Dike Swarm

The Egersund dike swarm intruded during the Neoproterozoic at  $616 \pm 3$  Ma, according to Bingen, Demaiffe, and van Breeman (1998) [3]. The dikes intruded the 0.93 Ga [2] Rogaland anorthosite complex and the surrounding Sveconorwegian granulite facies terrain. These dikes are subvertical [3], were emplaced along a WSW-ESE fault [4], trending  $110^\circ$  -  $120^\circ$  [3]. The Egersund dikes also appear to be subparallel to the southern Baltic shield. Therefore, the dike swarm must have been emplaced between the Baltic Shield to the north and Amazonia to the south [5].

Around 650 Ma, the initial rift-related magmatism of the Egersund complex began. The ocean basins formation began 630-620 Ma. The separation of Baltica and Laurentia was complete by 600 Ma. This rifting event feasibly included the rifting of Baltica and Amazonia. Moreover, the Egersund dikes were intruded along the southern rifted margin of Baltica [5].

## Map of Egersund Dikes of SW Norway



**Figure 2:** Map of the Egersund Dikes of SW Norway from which rock samples were taken. The Egersund Dikes are thought to have formed by a mantle plume during the initial stages of the breakup of the supercontinent Rodinia.

## Method

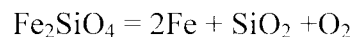
### Samples and Analysis

Two Egersund dikes were sampled and analyzed using the electron microprobe in the Microscopic and Chemical Analysis Research Center at The Ohio State University. USGS Mineral standards were used for the analysis.

Two samples, 105c and R6B are from different locations on the same trachybasalt dike. One sample, BRK1A is from a transitional dike of a composition between a trachybasalt and an olivine tholeiite (see Appendix for petrographic details).

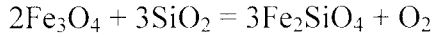
### Oxygen Fugacity

Iron exists in three oxidation states and has the potential to occur in a more oxidized or reduced state. Therefore, oxygen fugacity is used as a variable to indicate the potential for iron to occur in a more oxidized or reduced state in geologic systems. In meteorites and in the Earth's core, oxygen fugacities are very low. Iron (Fe) is present as a metal. In silica bearing systems oxygen fugacities are higher. Iron occurs as a divalent cation, and divalent iron is mostly incorporated into silicates. The reaction controlling this change is as follows [7]:

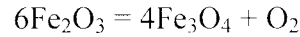


Iron is present both in the divalent ferrous iron ( $\text{Fe}^{+2}$ ) and the trivalent ferric iron ( $\text{Fe}^{+3}$ ) states at even higher oxygen fugacities. Nearly all of both forms are incorporated into magnetite.

The following reaction illustrates this change [7]:



Iron occurs in the ferric state in hematite at very high oxygen fugacities. Hematite forms magnetite according to the following reaction [7]:



### Olivine Melt Method

Oxygen fugacities were determined by using the olivine melt method developed by Michael Barton of the Department of Geological Sciences at The Ohio State University. Oxygen fugacity ( $f\text{O}_2$ ) is obtained by the relationship between  $\text{Fe}^{+3}/\Sigma\text{Fe}$  in the melt [7]

Olivine is the first mineral phase to crystallize out of basaltic melt of varying compositions. Olivine exists as a complete solid solution between forsterite,  $\text{Mg}_2(\text{SiO}_4)$  and fayalite,  $\text{Fe}_2(\text{SiO}_4)$ . The olivine is often observed to be more magnesium rich and more iron poor than the melt composition [8].

The distribution coefficient  $K_D = (\text{X}_{\text{FeO}}^{\text{Ol}}/\text{X}_{\text{FeO}}^{\text{Liq}})(\text{X}_{\text{MgO}}^{\text{Liq}}/\text{X}_{\text{MgO}}^{\text{Ol}})$  is independent of temperature.  $K_D$  defines the division of iron and magnesium in the relationship between olivine and melt. This equation allows for the prediction of the olivine composition as it crystallizes from a melt of a known ferrous iron and magnesium ratio. It also allows for the

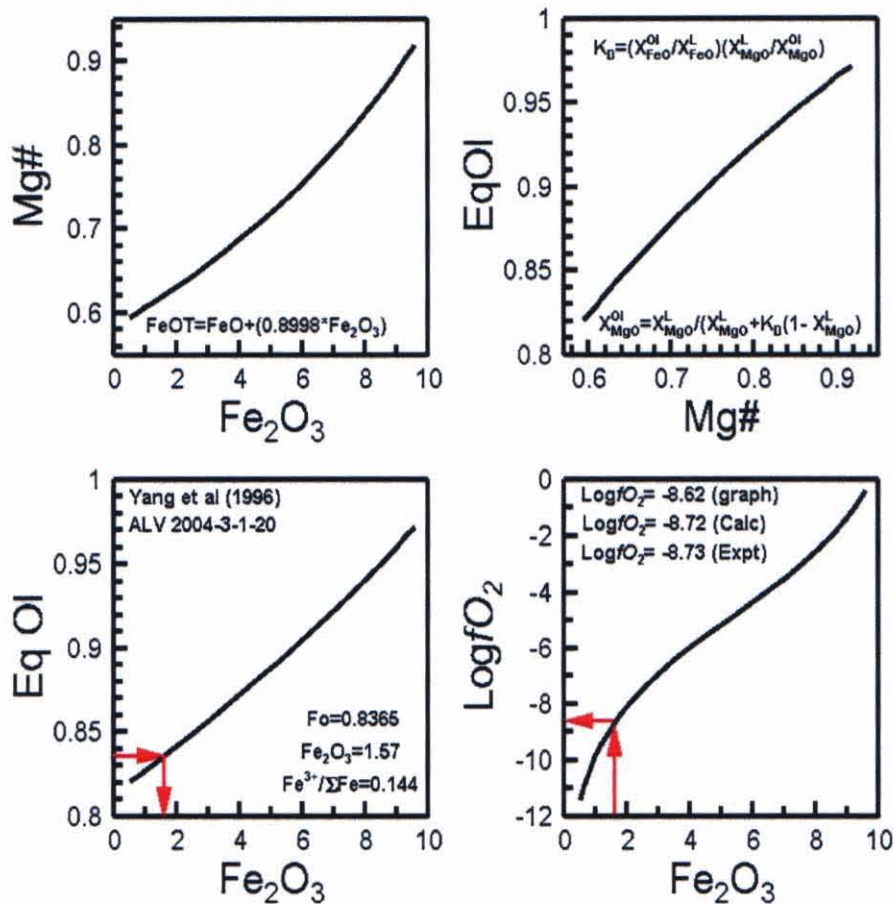
prediction of the liquid melt ferrous iron and magnesium ratio from an olivine of a known ferrous iron and magnesium composition [9].

The  $K_D$  value and Mg# can be used to determine a predicted olivine composition. This links the Mg# for the melt to the olivine. However, this is true only if the olivine crystal and the melt are in equilibrium. The measured values for MgO are used to determine the  $K_D$  [10] value. The  $K_D$  value is necessary to determine whether the olivine composition is in equilibrium with the melt. The method is illustrated in Figure 3.

### Redox State

Redox state of the mantle can be determined by using the oxygen fugacity of a mantle plume against the fayalite-magnetite-quartz buffer (FMQ). If the oxygen fugacity plots in the positive range, it is oxidized. However, if the oxygen fugacity plots in the negative range, it is considered reduced. If an oxygen fugacity is plots at zero, it is neither oxidized nor reduced according to the FMQ buffer.

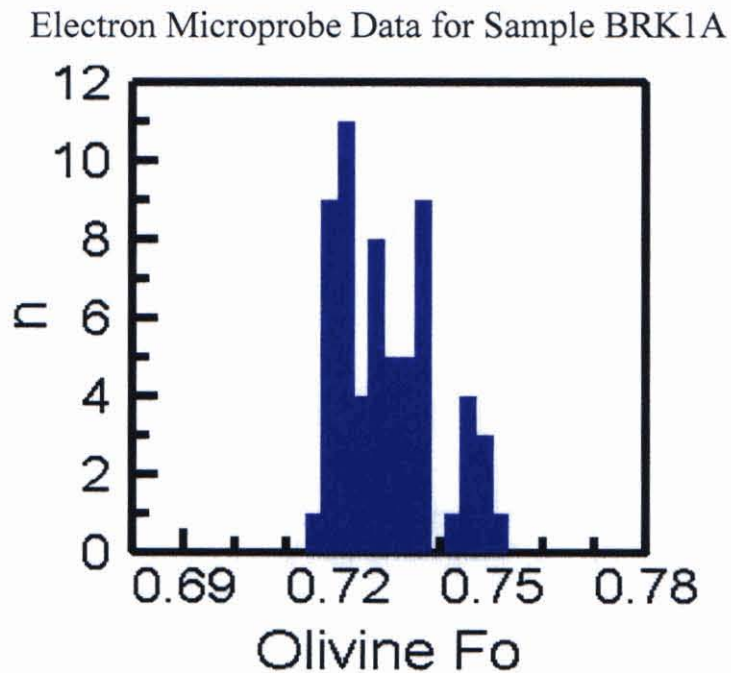
## Olivine Melt Method



**Figure 3:** The graphs display method for determining the oxygen fugacity, developed by Michael Barton, Professor for the Department of Geological Sciences, at The Ohio State University. The compositions and coexisting liquid can be used to determine  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$  in the melt.  $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$  can then be used to calculate  $\log f\text{O}_2$  by using the Kress and Carmichael (1991) equation [11]. The example shown is taken from the results of an experiments by Yang et al. (1996) [12]. The method relies on an accurate and precise  $K_D$  to predict olivine compositions in equilibrium with the melt as a function of  $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ . To calculate  $K_D$ , the Gee and Sack (1988) equation [10] was used. In 189 experiments at 0.1 MPa, values of  $f\text{O}_2$  calculated for equilibrium olivine-melt pairs were produced. These agree with reported values to  $\pm 0.22$  log-bar units,  $1\sigma$ .

## Results

The results of the analysis showed that the average olivine rim value is 0.7180. The majority of the rim values fall within  $\sim \pm 0.01$  point from the average value. The maximum values that are shown in figure 4 are expressing an olivine composition with a xenocryst signature. In other words, the olivine in question was not in equilibrium with the melt and was a foreign body picked up by the melt during emplacement.



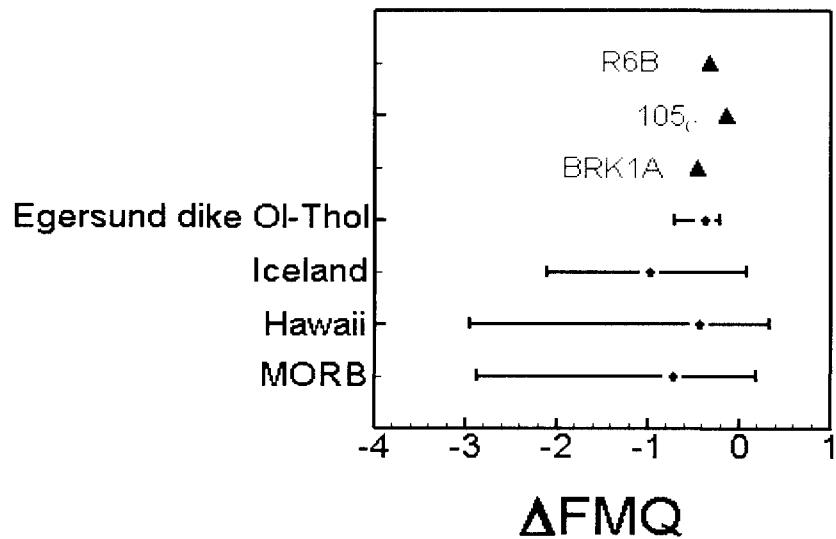
**Figure 4:** Histogram of olivine forsterite (Fo) plotted against the number of occurrences. Electron microprobe was used to determine the compositional zoning in olivine so that the compositions that were in equilibrium with the melt prior to eruption could be constrained. This primarily involves examining variations in Mg/Fe between core and rim in individual olivine crystals. The composition used is the average rim (Fo 0.7180).



## Discussion

Single rim values for the samples R6B, 105c, BRK1A are in equilibrium with the melt and are in agreement with the other data for the other Egersund Dikes, recent plumes (Iceland and Hawaii), and MORB. The oxygen fugacities of R6B, 105c, and BRK1A fit tightly with one another ( $\pm 0.3$  error) and with other Egersund Dikes, recent plumes (Iceland and Hawaii), and MORB. This clearly shows that the Egersund Dikes do express a mantle plume signature. In addition, the results for these samples also show that the redox state of the mantle was the same during the emplacement of the Egersund Dike swarm as it is today

Comparison of Oxygen Fugacities



**Figure 5:** Bar graph displays the results for BRK1 and 105 samples are in agreement with data for other Egersund Dikes, recent mantle plumes (e.g. Iceland and Hawaii), and MORB, although the compositions of the rocks are different.

## Conclusions

- The magma redox states are similar to those obtained for other samples from the same dike system (ongoing research at OSU).
- Results obtained for the samples examined in this study are not unusual, and the available data indicate that the magmas in this dike system crystallized over a narrow range of  $fO_2$ .
- The Egersund Dikes display a mantle plume signature.
- The redox state of the mantle has remained unchanged over the past 650 my. Therefore, volcanic degassing was not the cause of the increase in atmospheric oxygen ~600 Ma that led to the evolution of metazoans.

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## Appendix

### Petrographic Descriptions

#### Trachybasalt

**Sample 105c.** This is a chilled margin with plagioclase, olivine, and pyroxene phenocrysts occurring in a glassy matrix. The plagioclase crystals are euhedral, 0.1mm - 0.3mm in size. The plagioclase phenocrysts display polysynthetic twinning with an average extinction angle of 40°. The olivines are subhedral to euhedral, 0.05mm - 0.1mm in size and almost completely altered to mica. The pyroxenes are subhedral to euhedral, 0.05mm - 0.15mm in size and some are sector zoned. The phenocrysts are surrounded by a glassy matrix.

**Sample R6B.** This is a chilled margin similar to sample 105c. However, it contains a denser groundmass. It was collected from a different location on the same dike.

#### Transitional Basalt

**Sample BRK1A.** This is a chilled margin with plagioclase, olivine, and pyroxene phenocrysts occurring in a glassy matrix. The plagioclase crystals are euhedral to subhedral and are 0.06mm - 0.5mm in size. The plagioclase display polysynthetic twinning with an average extinction angle of 42°. The groundmass plagioclase are up to 0.04mm in size. The olivine crystals are euhedral and are 0.05mm - 0.3mm in size. The groundmass olivines are up to 0.02mm in size. The pyroxene crystals euhedral and are 0.05mm - 0.4mm in size, weakly pleochroic and are zoned. The groundmass pyroxenes are up to 0.02mm in size. The

groundmass also contains mostly skeletal opaques and pleochroic biotite. Small quartz veins of 1.5mm - 3mm in size are also present.

**Sample #: BRK1A at 100x**



**Sample #: 105c at 40x**

